SYNOPSIS OF THE Ph.D. THESIS

Chemical Combustion and Hydrothermal synthesis of $Ni_{1-x}Zn_xFe_2O_4/SrFe_2O_4$ and $Ni_{1-x}Zn_xFe_2O_4/BaTiO_3$ nanostructures: Structural, Electrical, Magnetic and Multiferroic properties

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❖ Introduction

Recently, due to development of electronic technology, the trends of miniaturization and excellent electromagnetic properties are the utmost requirements of materials to be used for different purpose and these have been and are being fulfilled by the materials called Composites [1-2]. For few years extensive research has been carried out on Multiferroic (MF) composite materials [3-4] which have been under the focus of researchers due to their potential applications in electronics technology (as magnetic–electric sensors in radio-electronics, optoelectronics, microwave electronics and transducers). In MF materials, magnetic and electric orders coexist simultaneously and the coupling between spin and charge degrees of freedom gives rise to a wide range of magneto electric phenomenon [5-7]. The control of polarization by applying magnetic fields or the magnetization by applying electric fields, which is known as the magneto electric (ME) effect, appears in the materials when the electric polarization and magnetic orders are coupled to each other [7,8].

The ME effect can also be given as direct ME effect which is characterized as magnetic-field-induced polarization and electric-field-induced magnetization, respectively [9]. The different types of single-phase multiferroic such as $BiFeO_3$ [9], $TbMn_2O_5$ [10], $BaTiO_3$-$CoFe_2O_4$ [11], 0.62Pb $(Mg_{1/3}Nb_{2/3})O_3$-0.38$PbTiO_3$ [12], $Ni_{47.4}Mn_{32.1}Ga_{20.5}$/PZT [13] etc. are investigated in reported work. Mostly these MF systems are extensively studied and they are the focus of current research because of the advancement in every field. To overcome the scarcity of single-phase multiferroic, one approach is to enhance the specific characteristics by doping or the other is the development of new Multiferroic materials such as ferroelectric-ferromagnetic. However the composite of ferrite such as $NiFe_2O_4$, $NiZnFe_2O_4$ and $CoFe_2O_4$ etc. with perovskite such as $BaTiO_3$, $PbTiO_3$and $CaTiO_3$ is of technological importance. Because these ferrites based composites are results in multiferroic properties of higher magnetization in spintronics devices. Also the electric behavior of ferrites is highly usable in high frequency based devices.

Ferrites continue to offer a rich display of a variety of physical phenomenon attracting physicist, chemists and material scientist. In composite materials, high ferrite content is needed to guarantee the requisite inductance. The synthesis of nanosize magnetic oxide particles, such as spinel nanoferrite of the type MFe_2O_4 (M is a divalent metal cation), are intensively investigated by researchers in terms of their applications in high-density magnetic recording media and magnetic fluids. These materials are also largely used in electric and electronic devices and in catalysis. In order to improve sinterability and magnetic properties, the

investigation of alternative, nonconventional synthesis methods to obtain ferrites in the form of nanostructured powders is the current subject [14-15].

Nickel ferrite, $NiFe_2O_4$ (NF) is an important member of the spinel family and it is found to be the most versatile technological materials suited for high-frequency applications due to its high resistivity [16]. In the bulk state, this material possesses an inverse spinel structure, in which tetrahedral (*A*) sites are occupied by Fe^{3+} ions and octahedral [*B*] sites by Fe^{3+} and Ni^{2+} ions. It exhibits ferrimagnetism that originates from the antiparallel orientation of spins on (*A*) and [*B*] sites. NF is a well-known spinel magnetic material having high resistivity and magnetostriction coefficient that give rise to a strong pseudo-piezomagnetic effect in a magnetic field [17].

❖ **Need of Research:**

The particles or grains in nanosize play a vital role in the improvement of properties of Multiferroic materials as compared to bulk *i.e.* low leakage current and show dielectric response up to higher frequency region. With the increasing demand of miniaturised/smaller, faster electronic devices, sensitive detectors for biomedical and environmental applications, it has become a necessity to synthesise materials in nano range < 100 nm.

Ferrites based composites have two advantages such as multiferroic as well as ferrite properties which are used in spintronics and high frequency electronic devices. To enhance ferrite properties there is need to combine some hard ferrite ($CoFe_2O_4$, $SrFe_2O_4$ etc.) with soft ferrite ($NiFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$ etc.). Therefore it is important to study best quality of ferrites for improved electrical and magnetic based applications and their composite with perovskite for fabricating MF materials.

Recent work on nanomaterials has revealed ME behaviour in $NiFe_2O_4/BaTiO_3$ systems, $NiFe_2O_4$/PZT, $NiCoFe_2O_4/Ba_{(0.8)}Pb_{(0.2)}TiO_3$ [18-19] and $NiFe_2O_4/Ba_{(0.8)}Sr_{(0.2)}TiO_3$ etc.$BaTiO_3$ [20] which shows these systems have high permittivity, low dielectric loss and high tenability whereas $NiFe_2O_4$ and $NiZnFe_2O_4$ are known for their chemical stability, high resistivity and excellent electromagnetic properties [21]. Composites of these materials and individually they need to be researched for further improvement and their possible applicability in different fields.

❖ **Methodology:**

There are several methods for preparation of nanomaterials Viz. Chemical vapour deposition, Physical vapour deposition, Sputtering, Hydrothermal, Co-precipitation,

chemical combustion method etc. [22-25]. Every method has its own impact on the properties of nano materials which depend upon various parameters. Among these we have selected/chosen Chemical combustion and hydrothermal method for the preparation because of their individual and distinctive features. Chemical combustion method produces nanoparticles with much ease and comfort, simple calculation, homogenous and un-agglomerated powder, inexpensive raw material. On the other hand hydrothermal method is a low temperature synthesis routes resulting in the fabrication of different nanostructures (in the form of nano rods, nano particles, nano wires, etc.) also provides ease in optimization of process parameters and restricts size to remain in between 1-20 nm which further enhances various properties of synthesised material.

The survey of literature indicates that there is still scope of research as only a lesser work has been reported on $Ni_{1-x}Zn_xFe_2O_4/SrFe_2O_4$ and $Ni_{1-x}Zn_xFe_2O_4/BaTiO_3$ system in both bulk and nano forms. The main aim and objective of the present plan of research work is to undertake a systematic studies on synthesising parameters and possibility of multifunctional properties i.e. structural, microstructural, magnetic, electric and dielectric properties in nanostructured $Ni_{1-x}Zn_xFe_2O_4$, $Ni_{1-x}Zn_xFe_2O_4/SrFe_2O_4$, $BaTiO_3$ and $Ni_{1-x}Zn_xFe_2O_4/BaTiO_3$ system by using Chemical combustion and Hydrothermal method. These methods are cheap, simple and provide free choice of the composition of components. So we have planned to involve both methods due to their unique features to investigate changes in properties by applying these methods. Further, these results can be useful to a large extent in giving new dimensions to the emerging technologies.

❖ **Important aspects of work:**

1) To chemically synthesize the nanomaterials of pure $NiFe_2O_4$ and doped with Zn and composite materials with $BaTiO_3$, and the enhancement in ferrite properties of $NiZnFe_2O_4$ with hard ferrite $SrFe_2O_4$. All the composition of these ferrite and multiferroic composite have been prepared by two methods: Chemical Combustion and Hydrothermal.
2) For combustion PEG (Poly Ethylene Glycol) is used as an efficient fuel and solvent and urea is used to create an overall redox system.
3) In hydrothermal synthesis, NaOH / NH_4OH / KOH have been used as a basic medium for pH adjustment.
4) Effects of particle size on the various properties of ferrite nanoparticles and Multiferroic nanoparticles have been investigated.

5) Comparative analyses of preparation methodology on properties of resulting materials have been investigated.

6) Effect of Zn concentration on the structural, Microstructural, dielectric and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$ system have been thoroughly investigated.

7) Effects of preparation of composite of $BaTiO_3$ and $SrFe_2O_4$ with $NiFe_2O_4$ and $NiZnFe_2O_4$ have been investigated.

❖ Experimental and Characterization details

The $Ni_{1-x}Zn_xFe_2O_4$, $Ni_{1-x}Zn_xFe_2O_4/SrFe_2O_4$, $BaTiO_3$ and $Ni_{1-x}Zn_xFe_2O_4/BaTiO_3$ systems have been synthesized by Chemical Combustion and Hydrothermal methods:

1) $NiFe_2O_4$ nanoparticles have been prepared by chemical combustion method at different temperatures.

2) $Ni_{1-x}Zn_xFe_2O_4$ nanoparticles has been prepared by chemical combustion method. (Where percentage of x has been taken in accordance with the resultant outcome).

3) $NiFe_2O_4/BaTiO_3$, $Ni_{1-x}Zn_xFe_2O_4/BaTiO_3$, $NiFe_2O_4/SrFe_2O_4$ and $Ni_{1-x}Zn_xFe_2O_4/SrFe_2O_4$ have been synthesized by chemical combustion method.

4) $NiFe_2O_4/BaTiO_3$, $Ni_{1-x}Zn_xFe_2O_4/BaTiO_3$, $NiFe_2O_4/SrFe_2O_4$ and $Ni_{1-x}Zn_xFe_2O_4/SrFe_2O_4$ have been prepared by hydrothermal method.

❖ Details of processing steps

(A) Processing steps used for preparation of materials by chemical combustion method

1. Analysis, purification of raw materials.
2. Checking feasibility of Stoichiometric ratios of constituent of different powders.
3. Processing of nanoparticles by chemical combustion method using PEG.
4. Crystallization and annealing of powdered samples, their washing and purification.
5. Pellet formation by pressing crystallized powder by using PVA as binder.

(B) Processing steps used for synthesis of materials by hydrothermal method

1. Analysis, purification of raw materials.
2. Checking solubility of stoichiometric ratios of different raw materials.
3. Processing of materials by hydrothermal treatment in an autoclave.
4. Crystallization and annealing of powdered samples, also their washing and purification.
5. Pellet formation by pressing crystallized powder by using PVA as binder.

❖ **Characterization steps for samples**

(A) Structural and microstructural parameters

(i) X- ray diffraction

(ii) Transmission electron microscopy

(iii) Scanning electron microscopy

(B) Magnetic properties

(i) Saturation magnetization.

(ii) Coercivity.

(iii) Phase transition temperature.

(iv) Low temperature magnetic hysteresis

(C) Optical properties

(i) Fourier Transform Infrared spectroscopy (FTIR).

(ii) UV-Visible spectroscopy

(D) Electrical properties

(i) Dielectric constant

(ii) Loss tangent

(iii) AC electrical conductivity

(iv) DC resistivity

(E) Multiferroic and magneto electric coupling

❖ **Measurement and Instrumentation Details**

All the series of the samples have been prepared at the Akal School of Chemistry and Physics, Eternal University, Baru Sahib, H.P and characterization was done at SAIF Panjab University, Chandigarh, USIC, University of Delhi, Delhi and National Physical Laboratory, New Delhi.

(A) Structural and Microstructural measurements

X-ray diffraction of samples has been carried out by using X-Pert PRO Panaltical system. The microstructural properties has been studied by Scanning electron microscopy using JEOL JSM 6100, Transmission electron microscopy has been investigated using Hitachi H-7500 at SAIF Panjab University Chandigarh.

(B) Magnetic and Electrical measurements

The magnetic permeability measurement has been performed by using a vibrating sample magnetometer (VSM-735) at NPL, New Delhi. The electrical measurements have been carried

out with an impedance analyzer (4200 semiconductor character unit, CVU module at NPL, Delhi. Both measurements have been carried out at room temperature. To carry out electrical measurements, the annealed powder was further mixed with PVA (binder) and pressed into pellets of thickness 0.5mm by using cold isotactic pressing method with a pressure of 5 bar for 5 min and was then subjected to sintering.

(C) Optical measurements

The transmission of light through nanostructured material for Fourier transform infrared spectrum (FTIR) and UV-Vis spectrum has been performed, measured and recorded on Perkin Elmer spectrum 400 FT-IR/FT-FIR spectrophotometer using triglyceride (TGS) detector and Perkin Elmer UV spectrometer λ 35* at SAIF, Panjab University, Chandigarh respectively.

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